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# **Creep Analysis of Poly(ester urethane) Copolymer by Dynamic Mechanical Analysis (DMA): Melt Determination**

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## **Abstract**

An experiment is presented utilizing film tension, creep test dynamic mechanical analysis (DMA) to characterize the physical properties of a poly(ester urethane) block copolymer, Estane<sup>®</sup> 5703. The polymer was pressed into a sheet from pellet form and cut into strips for analysis utilizing the TA Q800 DMA with film tension clamp. The strips were tested under five constant stress analyses from 0.125 to 0.625, at 0.125 MPa increments. Each analysis was run stepwise through a temperature gradient from 25 °C to 67.5 °C with 2.5 °C increments, the material reached the instrument maximum displacement at different temperature steps dependent on the constant applied stress. At each of the 18 temperature steps the material was held at constant stress for 10 minutes and allowed to recover under stress-less conditions for 20 minutes. With data analysis recoverable strain data was produced and ultimately a curve of Modulus at temperature, the regression extrapolated to modulus= 0 MPa. The extrapolated point correlated with data the weighted average melt point of the polymer measured by MDSC, within the regressive least squares fit of the measured moduli. Thereby measuring the melt temperature of a polymer by DMA. This is the third in a series of three reports<sup>4,5</sup> on the physical properties and degradation processes of materials used in polymer bonded explosive 9501 written for submission to the University of Oregon, Masters Industrial Internship Program.

## **Introduction**

Poly(ester urethane) (Figures 1 & 2) is used in conjunction a eutectic mixture of bis-2,2-dinitropropyl acetal and bis-2,2-dinitropropyl formal (known as Nitroplasticizer, NP) (Figure 1b) as binder materials for polymer bonded explosives (PBX).<sup>2,6</sup> By using Poly(ester urethane)/NP as binder, the composite with 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) is more resistant to catastrophic insult compared with neat HMX.<sup>4,5,7-10</sup> The resulting PBX composite material can be machined while remaining a highly effective explosive material.<sup>6</sup> Because of the direct correlation of polymer chain length with mechanical properties of PBX<sup>1-3,11-13</sup>, polymer degradation rates are critical for the safe use of the material.<sup>10</sup> Estane<sup>®</sup> 5703 poly(ester urethane) block copolymer (called Estane hereafter), used in PBX 9501, a material utilized in many Department of Energy projects. To properly establish baseline physical characteristics of Estane and in ultimately PBX, a suite of analytical techniques has been applied to pristine Estane. The Estane sample can be called pristine as it has been stored in a -1 °C freezer since manufacture.

Inclusive of the pristine sample, Estane samples have been analyzed by gel-permeation chromatography (GPC) to determine their molecular weights, thermo-gravimetric analysis (TGA) to establish thermal stability, and modulated differential scanning calorimetry (MDSC) to determine glass transition temperatures ( $T_g$ ), melt temperature(s) ( $T_m$ ), and specific heat capacity (RevCp). Additionally, they have been analyzed by Fourier transform infrared attenuated total reflectance (FTIR-ATR), and Raman spectroscopy to correlate spectroscopic data with molecular mass and aging degradation products. Analysis of the pristine sample by DMA film tension creep will be used in conjunction with the various other analyses listed to create a baseline set of physical and chemical properties, which in later studies will be compared with either naturally or artificially aged Estane samples.

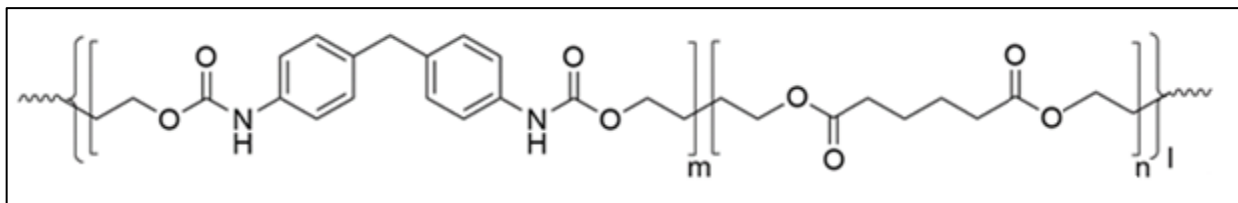


Figure 1: Generalized structure of Estane<sup>®</sup> 5703, rigid section is denoted with repeat unit  $m$  and is defined as approximately 23% by weight<sup>1,2</sup>, modified figure from Salazar et al (2002)<sup>3</sup>

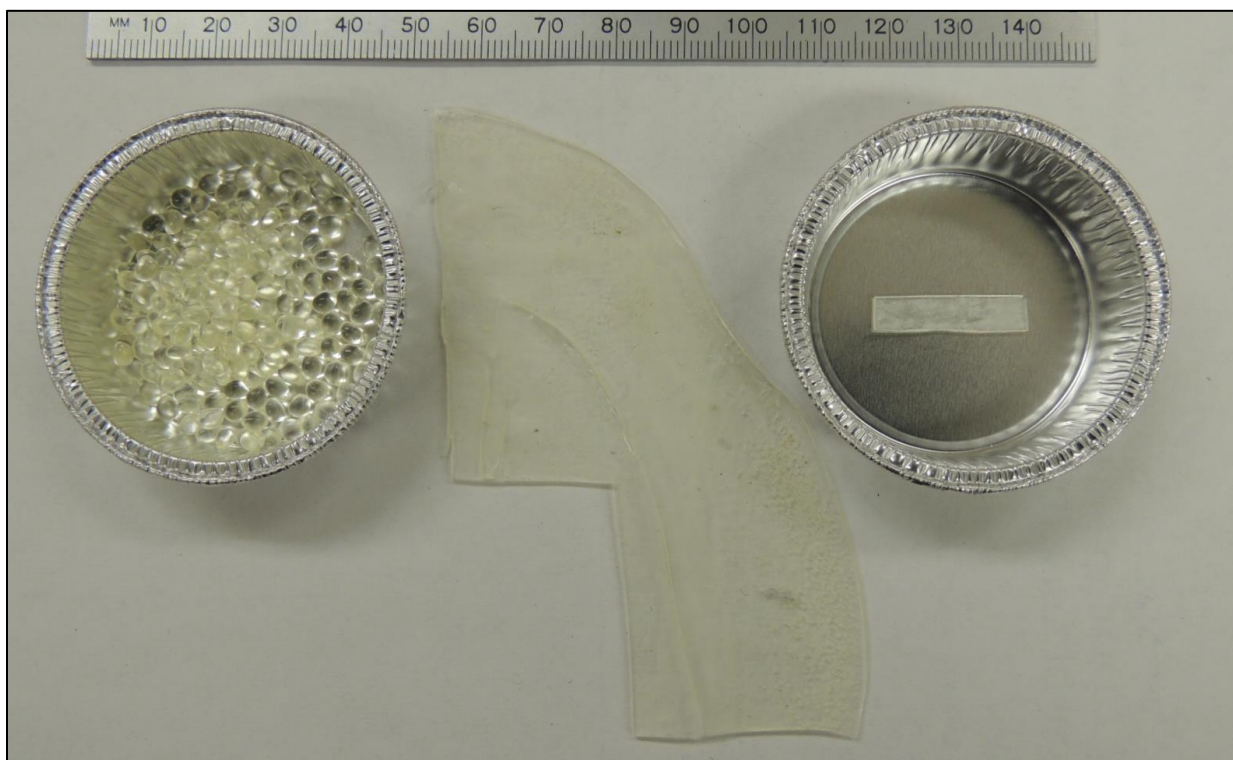


Figure 2: Photograph of Estane polymer beads, partial sheet, and cut strip of analysis by film tension DMA. The sheet shows wrinkles and bubbles.

## **Background**

DMA is a valuable tool for determining mechanical or rheological properties of a material as a function of time, frequency, temperature, stress, and strain. DMA is particularly well suited to determine the properties of visco-elastic polymeric materials. DMA has multiple types of clamps, enabling analysis of samples in various geometries. Clamp geometries include: dual/single cantilever, 3-point bend, compression plate, shear sandwich, fiber tension, film tension, powder, and submersion clamps. All of the clamps either produce unique data. For example the compression clamp produces bulk moduli, the shear sandwich produces shear moduli. Further, clamps are suited to particular sample characteristics. An example is the dual cantilever clamp which could be used for a bar shaped sample of low stiffness, the single cantilever can be used for a bar shaped sample of high stiffness. The versatility of DMA is even further increased by applying multiple types of tests (strain sweep, frequency sweep, creep/constant strain, etc.) to the multiple clamp geometries.

DMA measures two raw signals: force, and deformation. All mechanical parameters of the material are calculated from these two raw signals (equations 1, 2, & 3)

$$\text{eqn. 1} \quad \text{Stress (Pa)} = \frac{\text{Force (N)}}{\text{Area (m}^2\text{)}}$$

$$\text{eqn. 2} \quad \text{Strain} = \frac{\text{Deformation (m)}}{\text{Length (m)}}$$

$$\text{eqn. 3} \quad \text{Modulus (Pa)} = \frac{\text{Stress (Pa)}}{\text{Strain}}$$

From the two raw signals measured by DMA, with sample size measured by caliper, temperature controlled by Bifilar-Wound furnace and measured by thermocouple, many material parameters can be calculated including: moduli (Storage/Elastic, Loss/Viscous, Young's, Shear, Bulk), damping factor ( $\tan \delta$ ), compliance, thermal transitions ( $T_g$ ,  $\beta$ ,  $\gamma$ ), stiffness, stress, and strain. For this experiment the film tension clamp was used for stepwise-temperature increment, creep tests.

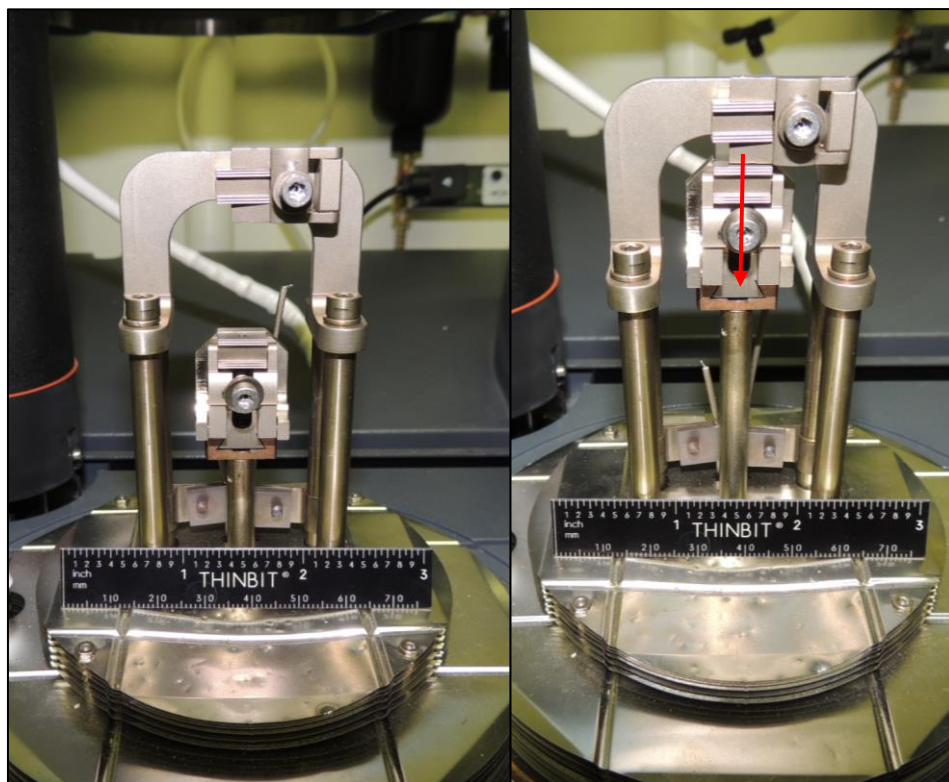
## **Experimental**

### ***Sample preparation:***

From the time of manufacture a pristine Estane bead sample was stored in a freezer at -1 °C until being pressed into a sheet using a Carver Model 3467 Heated Hydraulic Press for various analyses. 29.98 g of Estane was placed in 70°C oven for 10 minutes, and immediately pressed for 10 minutes at 149 °C under no load, then pressed for 20 minutes at 149 °C under 14.5 metric ton load. The resulting polymer sheet was cut into strips to fit the film tension clamp, strips were approximately 20mm x 8mm x 1mm (Length x Width x Thickness) see Figure 2.

***DMA Experiment:***

The experiment was conducted using the TA Instruments DMA-Q800. The thickness and width of the strips were measured by caliper, length was measured by the DMA. In a creep recovery experiment, constant stress ( $\sigma$ ) was applied for 10 minutes then released for 20 minutes while monitoring strain ( $\epsilon(t)$ ) at various temperatures. The testing started at 25°C and increased to 67.5°C in 2.5°C increments. After calibrating the DMA film tension clamp for clamp mass, position, and compliance (movement), samples were fixed to the clamp using 4 ft. lbs. of torque on clamping mechanism. The samples were run using fixed strains for the displacement portions of the experiment, the fixed strains were individual to each sample, and included 0.125, 0.250, 0.375, 0.500, and 0.625 MPa.



*Figure 3: TA Instruments Film tension clamp attached to Q800 DMA, Left: fully extended movable clamp no Estane in clamp, Right: Estane loaded in clamp, arrow indicates direction of clamp movement when test is run under constant force.*

## Results and Discussion

The raw data were plotted in Figures 4 & 5. Local maxima, local minima, and slopes were evaluated, maxima and minima are indicated by arrows in Figure 4. Strain maxima (%) were determined for each 30-minute temperature step, the maxima was consistently found to be the last moment of the 10 minute constant stress regime in each step. Unrecoverable strain (%) was determined to be the minima of each 30 minute temperature interval, the minima was not always the last moment of the relaxation portion of the interval, however in each instance it was in the 20 minute relaxation portion the step. Creep rate (%/min) was interpreted as the slope of the linear region of the time vs strain curve in the constant stress portion. Recoverable strain was calculated by subtracting the unrecoverable strain from the strain maxima. These four signals are plotted against temperature in Figure 6.

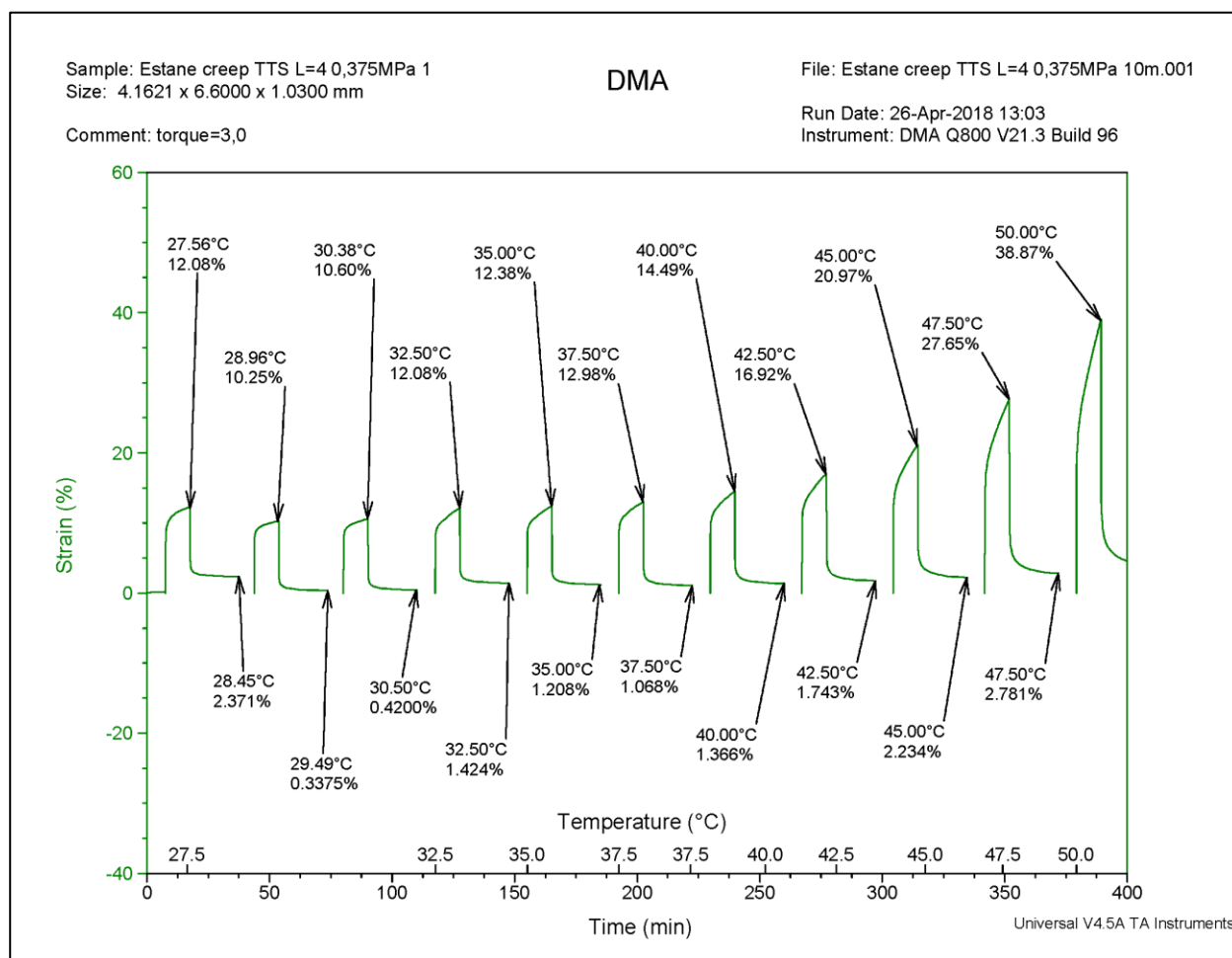


Figure 4: Strain (%) signal produced from the 0.125 MPa strain run of Estane.

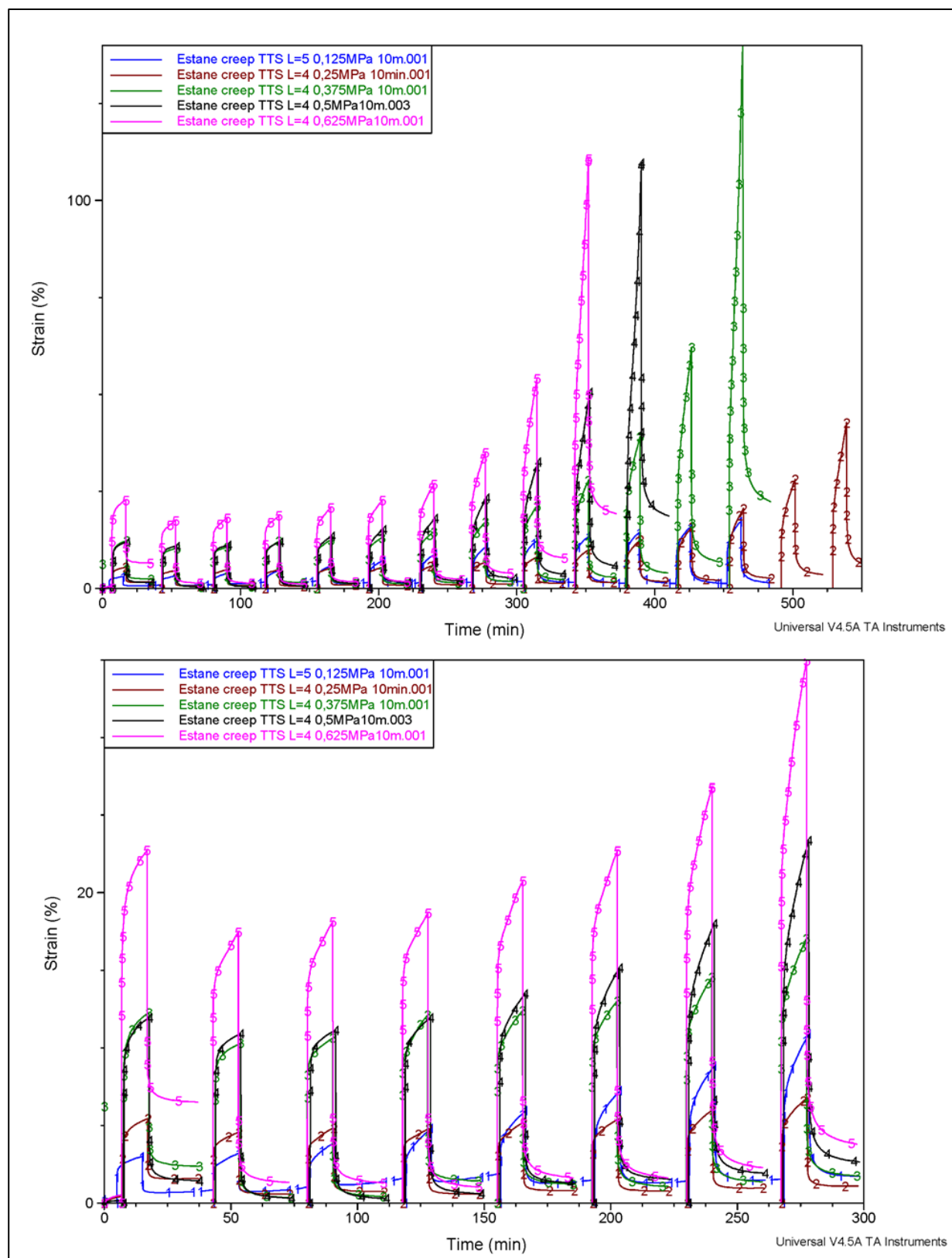


Figure 5: Overlay of strain (%) signals produced from all Estane creep method tests. Full scale top and zoomed on lower temperature steps bottom.



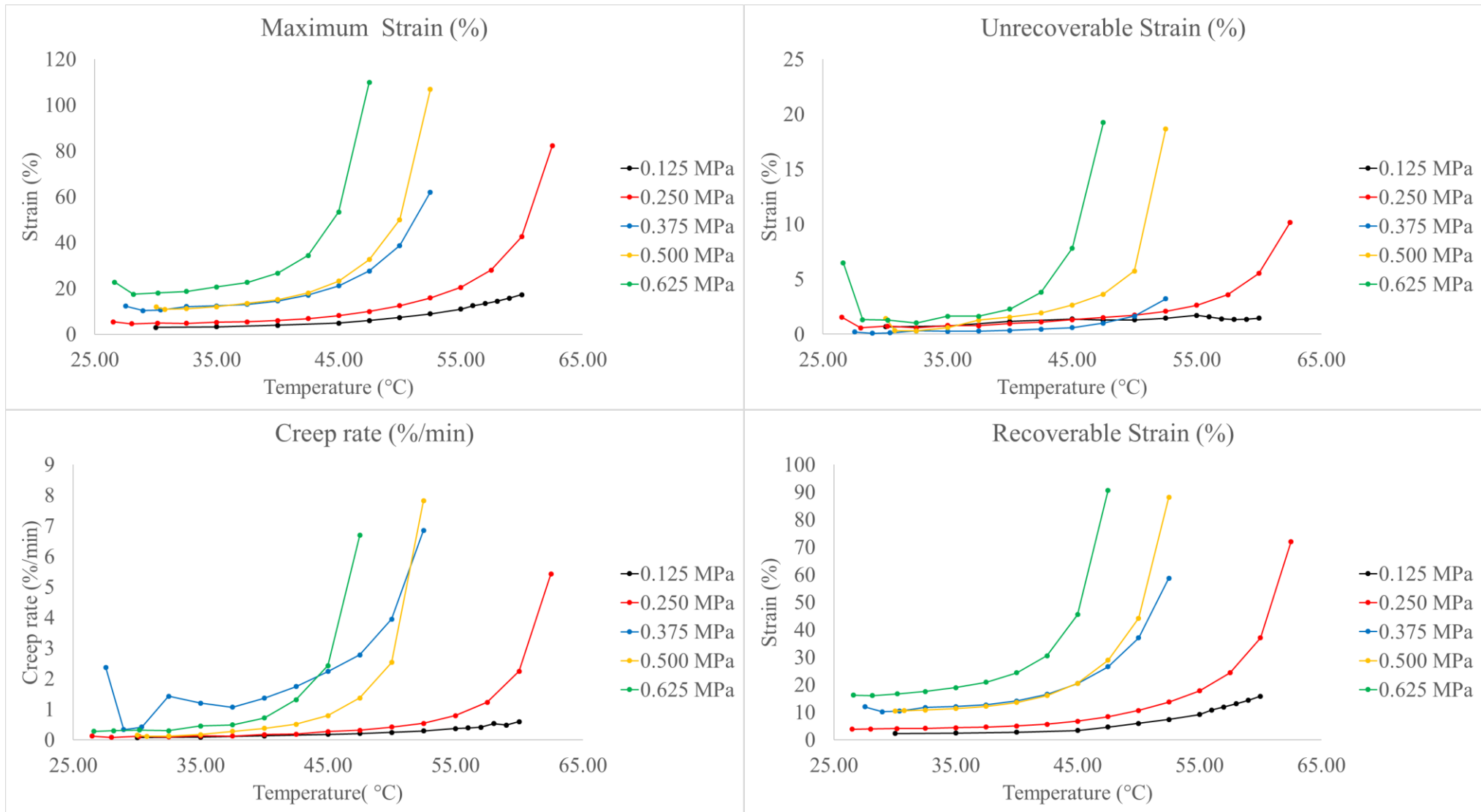


Figure 6: Four graphs produced by the creep tests, clockwise from top left: Maximum strain are local maxima for each constant stress at temperature increment, Unrecoverable strain are local minima for each stress=0 at temperature increment, recoverable strain is the difference between maximum strain and unrecoverable strain, and creep rate is the slope of strain in the linear region of the constant stress at temperature incremental step.

The trends among the resultant data (Figure 6) are similar, despite differences in magnitude. The material shows increasing maximum strain, unrecoverable strain, creep rate, and recoverable strain with increasing temperature which is consistent with the expected results. The Estane strip analyzed at 0.375 MPa outlies the trends among the other data points, it is expected the abnormality of the data is the result of an irregular void space (a bubble) or an abnormal induced stress (a wrinkle) in the strip. As seen in the previous iteration of this series of papers in which Estane calorimetry is explored,<sup>5</sup> Estane physical and thermal properties can be greatly influenced by thermal history including annealing time and temperature.<sup>1-5,8,9,12-14</sup> It is possible that annealing conditions are different enough in the center and edge of the sheet that it effected the creep analysis of the strip used for the 0.375 MPa stress measurement. For these suspected issues with the sample strip the data of 0.375 MPa has been omitted from the calculations leading to the subsequent conclusions in this paper.

Excepting the outlying 0.375 MPa sample, each sample had a significant decrease in maxima strain and unrecoverable strain on the second temperature step of the method, this trend was attributed to the thermal/physical erasure of induced strain in the material from the sheet pressing process. Following the reduction in minima, proxy to thermal history being reduced to negligible, the data clearly show a trend of increasing strain with increasing temperature (Figure 6). From the calculated recoverable strain, plots of stress vs strain were generated at eight temperatures, as shown in Figure 7, the data is tracked with a spline to show the general trend. The slope between the lowest two temperatures is used as proxy for Young's modulus, referred to as modulus. Further, the derived moduli were plotted vs temperature and fitted with a linear least squares regression extrapolated to Modulus  $\cong 0$ , and temperature  $\cong 0$  (Figure 8).

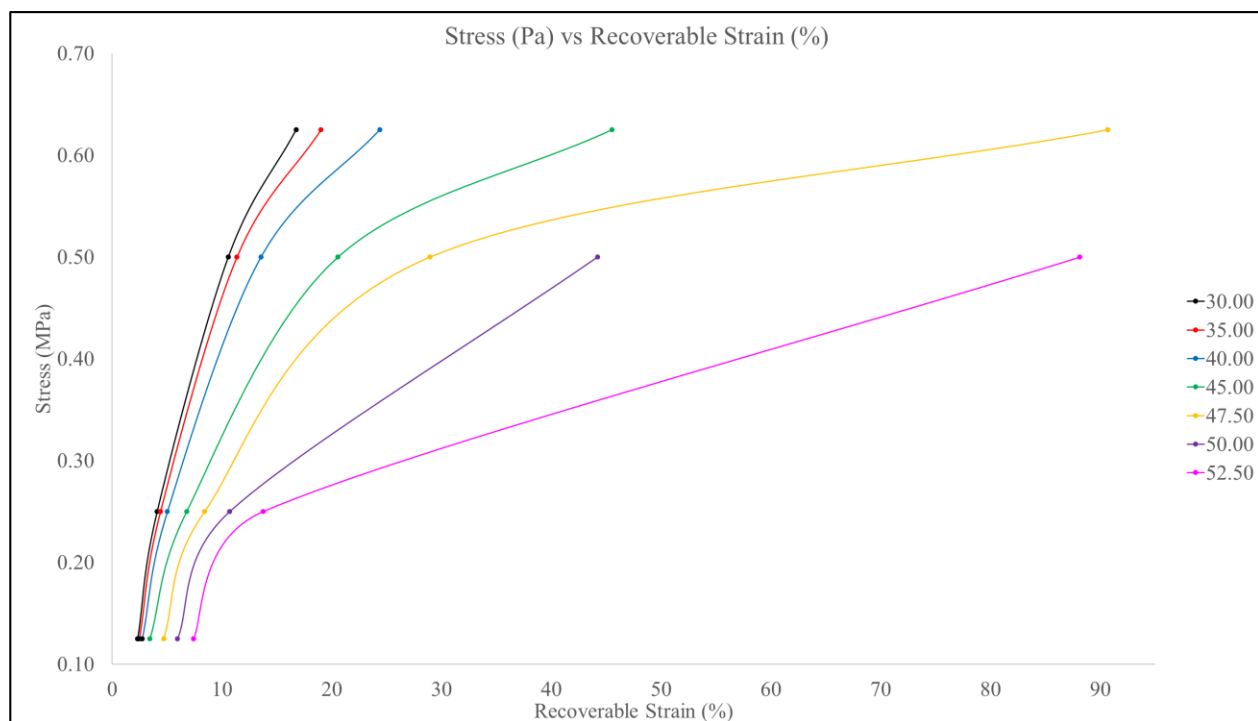


Figure 7: Stress vs strain spline fits at eight temperatures, linear portions of slope of lower stress points are proxy to Young's Moduli.

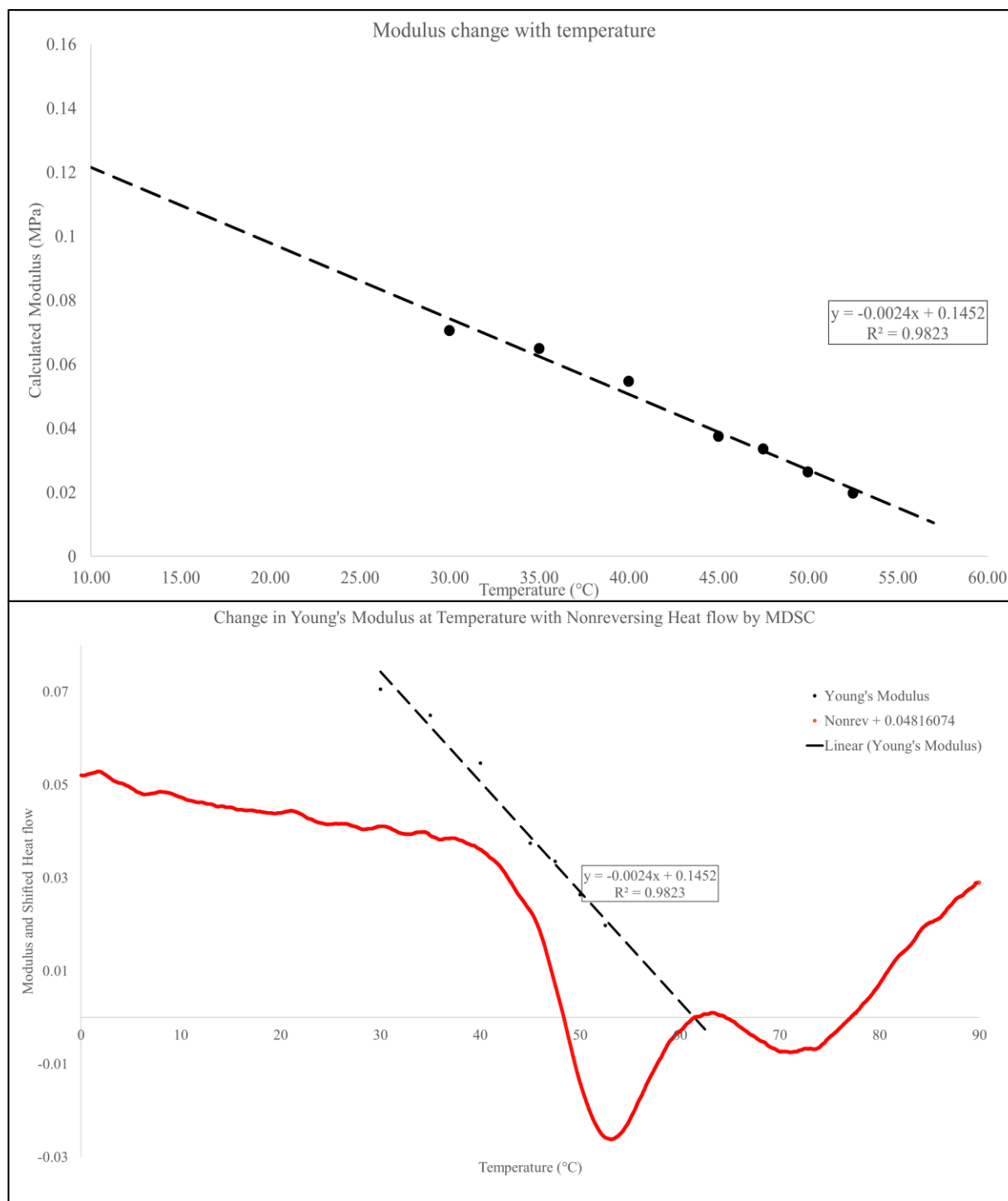


Figure 8: Top: Moduli calculated from the lowest two stress points from Figure 7 at temperature, linear least squares regression extrapolated to Modulus= 0. As expected, the modulus of Estane increases as the temperature decreases. At 0 °C, the Young's modulus of the sample reaches 0.1452 MPa (not shown graphically). Bottom: Moduli at temperature overlaid with MDSC signal of Nonreversing Heat Flow of the same sample of polymer, data was used from the experiments of the previous installment of this series, vertical shift factor of 0.04816074 was applied to the MDSC curve to illustrate the intersection point,  $T = 61.4$  °C.

Where temperature  $\cong 0$  °C, the phase of water in the polymer will change and the physical response of the material as a whole will change, predictions as the changes beyond this point are outside of the scope of this paper. However, where modulus  $\cong 0$  MPa, correlates with the thermal transition model presented in the previous installment of this series (Figure 8). By the heat only MDSC method detailed in the previous paper<sup>5</sup> the weighted average melt phase transition endotherm peak (long range and short range crystal disruptions)<sup>15</sup> for this specific polymer (pellet form) was calculated as 60.7 °C. Extrapolating the Modulus to 0 MPa yields 61.4 °C as the melt temperature of the material, which yields 1.1% difference, falling falls within the 1.8% error of the least squares regression fit.

The regression technique for the determination of melt temperature by DMA detailed above may be a novel approach to determining the approximate melt temperature by DMA, if the method proves novel it deserves attention to determine the accuracy of the method using known standards and a larger dataset. Although, the extrapolated melt temperature by DMA does correlate with the weighted average melt temperature determined by MDSC, it is dubious to state the DMA method will be accurate to determine melt. The results of this method help us to understand which of the melting events illustrated in Figure 8 dominate the melt transition and could even provide evidence to the effectiveness of annealing time. However, the result could be coincidental and warrants more testing to confirm the results.

## **Conclusion**

By determining baseline polymer characteristics this project has created a path for the future work of determining the physical characteristic changes in naturally or artificially aged Estane samples. In this future work the polymer will be exposed to multiple variants of natural environments and analyzed by a variety of spectroscopic, thermal analysis, and chromatographic techniques and will of course be analyzed by film tension creep DMA. In the future work the samples will be run in triplicate analyses to reduce the influence of outlier data derived the irregularities or induced stress in the polymer sheets. Although this work may be esoteric in terms of material, the methodology may ultimately be applied to many polymers, particularly in the case of copolymers or block copolymers, in which melt temperatures signals by DSC and MDSC may be erratic and require further verification.

If this melt determination portion of this experiment is in fact novel, it will be recreated with polymer standards. Using a standard with known melt temperature will provide a higher degree of certainty in determining the accuracy of the method against DSC or MDSC. DMA is currently used as an accurate technique in determining glass, beta, and gamma transitions, perhaps with further method analysis and development DMA could prove to be an accurate tool to measure the events that comprise melt transitions.

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